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compatible, in which, by means of contact with a vapor or liquid, and/or by means of application of an energy source (1) a coating is applied to the surface of an article, (2) chemical species are adsorbed onto the surface of an article, (3) the chemical nature (e.g., electrostatic charge) of chemical groups on the surface of an article are altered, or (4) the surface properties of an article are otherwise modified.

There are a variety of methods disclosed in the art for rendering a surface of a material hydrophilic. For example, the lens may be coated with a layer of a hydrophilic polymeric material. Alternatively, hydrophilic groups may be grafted onto the surface of the lens, thereby producing a monolayer of hydrophilic material. These coating or grafting processes may be effected by a number of processes, including without limitation thereto, exposing the lens to plasma gas or immersing the lens in a monomeric solution under appropriate conditions.

Another set of methods of altering the surface properties of a lens involves treatment prior to polymerization to form the lens. For example, the mold may be treated with a plasma (i.e., an ionized gas), a static electrical charge, irradiation, or other energy source, thereby causing the prepolymerization mixture immediately adjacent the mold surface to differ in composition from the core of the prepolymerization mixture.

A preferred class of surface treatment processes are plasma processes, in which an ionized gas is applied to the surface of an article. Plasma gases and processing conditions are described more fully in U.S. Pat. Nos. 4,312,575 and 4,632,844, which are incorporated herein by reference. The plasma gas is preferably a mixture of lower alkanes and nitrogen, oxygen or an inert gas.

In a preferred embodiment, the lens is plasma treated in the presence of a mixture of (a) a C_{1-6} alkane and (b) a gas selected from the group consisting of nitrogen, argon, oxygen, and mixtures thereof. In a more preferred embodiment, the lens is plasma treated in the presence of a mixture of methane and air.

IV. UTILITY

A. Ophthalmic Lenses

The novel polymers or crosslinked polymers can be converted into ophthalmic moldings in a manner known in the art, in particular into contact lenses, for example by carrying out the photopolymerization or photocrosslinking of the novel polymers in a suitable contact lens mold. Examples of novel ophthalmic moldings, in addition to contact lenses, include without limitation thereto, contact lenses for vision correction, contact lenses for eye color modification, ophthalmic drug delivery devices, ophthalmic wound healing devices, and the like.

B. Contact Lenses

A specific embodiment of the invention is directed to contact lenses which comprise essentially a novel polymer or polymeric network. Such contact lenses have a range of unusual and extremely advantageous properties. Amongst these properties are, for example, their excellent compatibility with the human cornea (if necessary after suitable surface treatment (coating)) and with tear fluid, which is based on a balanced ratio between water content and water permeability, oxygen permeability and mechanical and adsorptive properties. This balance of desirable properties results in high comfort and the absence of irritation and allergenic effects. Owing to their favorable permeability properties with respect to various salts, nutrients, water and diverse other components of tear fluid and gases (CO_2 and O_2), the novel contact lenses have no effect, or virtually no effect, on the natural metabolic processes in the cornea. In

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contrast to many other siloxane-containing contact lenses, the present innovative extended-wear lenses have chemical and mechanical properties and ion permeability sufficient to avoid the undesired binding effect. Furthermore, the novel contact lenses have high dimensional stability and shelf life.

It must be emphasized that this balance of properties, especially the high ion permeability in combination with the high oxygen permeability, is key to producing a true extended-wear contact lens. The high oxygen permeability is required to prevent corneal swelling, thereby reducing the likelihood of ocular damage and wearer discomfort during periods of extended wear. The high ion permeability enables the lens to move on the eye such that corneal health is not substantially altered and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids.

The preferred extended-wear contact lenses of the present invention are those which are comfortable over the period of extended wear. If the lens diameter is too small, the eyelids will not cover any portion of the lens when the eye is open. Thus, the eyelids will contact the edge of the lens each time the eyelid is closed. This repeated eyelid-lens interaction typically causes irritation, wearer discomfort, and lens dislodgement. Accordingly, the preferred contact lens diameters are those which are sufficiently large to minimize eyelid-lens interaction and the associated irritation. Preferably, the contact lens has a diameter of about 12 to about 16 millimeters, more preferably about 13 to 15 mm, and most preferably about 13.5 to 14.8 mm.

V. METHODS OF USE AS EXTENDED-WEAR LENSES

The above-described ophthalmic lenses have special utility as extended-wear contact lenses. Contact lenses having sufficient oxygen and water transmission rates from inner (base curve) to outer (front curve) surface may be continuously worn for long periods of time without substantial cornea swelling or wearer discomfort. The method of wear includes (a) applying the lens to the eye and (b) allowing the lens to remain in intimate contact with the eye and tear fluids for a period of at least 24 hours without substantial adverse impact on cornea health or wearer comfort.

A preferred method includes additional steps of (c) removing the lens from the ocular environment; (d) treating the lens (i.e., disinfecting or cleaning the lens); (e) re-applying the lens to the eye; and (f) allowing the lens to remain in intimate contact with the eye and tear fluids for a period of at least an additional 24 hours without substantial adverse impact on corneal health or wearer comfort.

In a preferred embodiment, the lens is worn for a continuous period of at least four (4) days without substantial corneal swelling or wearer discomfort. In another preferred embodiment, the lens is worn for a continuous period of at least seven (7) days without substantial corneal swelling or wearer discomfort. In another preferred embodiment, the lens is worn for a continuous period of at least 14 days without substantial corneal swelling or wearer discomfort. In yet another preferred embodiment, the lens is worn for a continuous period of at least 30 days without substantial corneal swelling or wearer discomfort.

VI. METHODS OF MANUFACTURE

The ophthalmic lens may be manufactured, generally, by thoroughly mixing the oxyperm and ionperm polymerizable materials, applying an appropriate amount of the mixture to a lens mold cavity, and initiating polymerization. Photoinitiators, such as those commercially available photoinitiators disclosed above, may be added to the prepolymerization mixture to aid in initiating polymerization. Polymerization may be initiated by a number of well known

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techniques, which, depending on the polymerizable material, may include application of radiation such as microwave, thermal, e-beam and ultraviolet. A preferred method of initiating polymerization is by application of ultraviolet radiation.

It has been discovered that the ion and/or water permeability of some of the aforementioned core materials may be increased by initiating and completing polymerization in an atmosphere which is substantially free of oxygen. Suitable gases which are readily commercially available include, without limitation thereto, nitrogen and carbon dioxide. Thus, in a preferred embodiment, the oxyperm and ionoperm polymerizable materials are polymerized in an atmosphere having less than about 10000 ppm oxygen. More preferably, the atmosphere surrounding the polymerizable material contains less than about 1000 ppm oxygen. Even more preferably, the surrounding atmosphere contains less than about 100 ppm oxygen, while the most preferred oxygen content is less than about 20 ppm.

In the aforementioned embodiment, the prepolymer mixture must be degassed prior to polymerization. The degassing may be accomplished by a number of techniques known in the art. One technique for degassing the prepolymer mixture involves the use of a series of freezing and thawing steps which are repeated until the appropriate gas concentration level is achieved in the prepolymer mixture. This freeze/thaw method involves cooling the prepolymer mixture until the mixture solidifies, applying a vacuum to the solidified prepolymer mixture, discontinuing the vacuum, and thawing the prepolymer mixture until the mixture is again in liquid form. While this degassing technique is advantageous in a laboratory setting, other degassing techniques known in the art may be more advantageous for commercial lens manufacturing processes.

Alternatively, the atmosphere surrounding the lens mold may include oxygen, under certain conditions. For example, if the lens mold halves seal adequately to one another and the lens mold material has a low rate of oxygen permeability (e.g., polypropylene), it is possible to polymerize a degassed prepolymer mixture in a mold surrounded by ambient air without reaching prepolymer oxygen concentrations sufficiently high to substantially reduce ion or water permeability of the final lens. Thus, in another preferred embodiment of double-sided molding, the lens is formed by the following steps: (1) the prepolymer mixture is degassed, (2) a lens mold half is filled with the prepolymer mixture, (3) the mold halves are sealed to one another, and (4) the polymerization is initiated to form the lens, where the lens mold halves are formed from a material having a low oxygen permeability and steps (2)-(4) may occur in the presence or absence of oxygen. In this embodiment, it is preferred that the lens molds are stored in an inert substantially oxygen-free atmosphere, e.g., nitrogen or carbon dioxide, prior to use.

An essential feature of the manufacturing methods of the present innovative lenses is that a balance of high oxygen permeability and high ion permeability is achieved. Manufacturing techniques and conditions which result in lowering either the oxygen permeability or the ion permeability below levels sufficient to maintain good corneal health and on-eye movement during periods of extended wear are unacceptable to produce the innovative extended-wear contact lenses of the present invention.

Preferably, the manufacturing method produces a contact lens having a Dk/t of at least 70 barrers/mm and a Ionoton Ion Permeability Coefficient of at least 0.2×10^{-6} cm²/sec. More preferably, the manufacturing method produces a contact lens having a Dk/t of at least 75 barrers/mm and a

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Ionoton Ion Permeability Coefficient of at least 0.3×10^{-6} cm²/sec. The manufacturing method preferably provides a contact lens having a Dk/t of at least 87 barrers/mm and a Ionoton Ion Permeability Coefficient of at least 0.4×10^{-6} cm²/sec.

The previous disclosure will enable one having ordinary skill in the art to practice the invention. In order to better enable the reader to understand specific embodiments and the advantages thereof, reference to the following examples is suggested. However, the following examples should not be read to limit the scope of the invention.

Examples A-D are arranged in accordance with the materials defined above. Thus, Examples A-1, A-2, etc. relate to Material "A" as defined above, Examples B-1, B-2, etc. relate to Material "B" as defined above, Examples C-1, C-2, etc. relate to Material "C", and Examples D-1, D-2, etc. relate to Material "D". Temperatures are stated in degrees Celsius unless otherwise specified.

Examples E, F and G are directed to demonstrating a correlation between on-eye movement and the Ionoton Ion Permeability Coefficient, the Ionoflux Ion Permeability Coefficient, and the Hydrotell Water Permeability Coefficient, respectively.

EXAMPLE A-1

A polysiloxane macromer is prepared by reacting, at room temperature (about 21 C.), one mole equivalent (about 100 grams) of poly(dimethylsiloxane)dialkanol (Shin Etsu Chemical Co., Tokyo, Japan) having hydroxyethyl propoxy end groups with 2 mole equivalents (about 21.2 grams) of isophorone diisocyanate (Aldrich Chemical Co., Milwaukee, Wis.) in the presence of about 0.2 grams dibutyltin dilaurate catalyst (Pfaltz & Bauer, Inc., Waterbury, Conn.). After about 48 hours reaction time, 2.02 mole equivalents (about 38.7 grams) of poly(ethylene glycol) ("PEG", about 610 g/mol Mn, Dow Chemical Corp., Midland, Mich.) and about 0.17 grams of dibutyltin dilaurate (about 0.43% by weight PEG) are added to 80 grams of the reaction product from the prior step. Sufficient chloroform (Aldrich Chemical Co.) is added to the mixture to make the mixture homogeneous. This mixture is stirred at room temperature for about 15 hours. Next, the mixture is stirred for about 8 hours at a temperature of about 44 to 48 C., with the temperature held substantially constant by a surrounding oil bath. The chloroform is then evaporated, in order to achieve a final concentration of about 50% by weight solids, by stirring the mixture at room temperature for about 8 hours. Then, about 2.14 mole equivalents (about 10.4 grams) of isocyanatoethyl methacrylate ("IEM", Monomer Polymer, Inc., Feasterville, Pa.) is added to the mixture. Finally, the mixture is covered with aluminum foil and stirred at room temperature for about 17 hours, yielding a polysiloxane-containing macromer having a number-average molecular weight (Mn) of about 4000 grams per mole.

The macromeric solution is then polymerized, in the presence of about 0.5 weight percent DAROCUR® 1173 photoinitiator (Ciba-Geigy Corporation, Ardsley, N.Y.) to form contact lenses. Polypropylene contact lens molds are filled with the copolymer precursor solution. Ultraviolet light (about 300 to 400 nm) at about 3-6 mW/cm² is applied to the solution in the mold for about 3 hours at room temperature. The UV light, in conjunction with the photoinitiator, causes polymerization, thereby allowing the solution to form a contact lens having the shape of the mold. The lenses are extracted with isopropanol to remove the remaining chloroform solvent and any unreacted components. The product is a polysiloxane-containing polymeric contact lens.

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Prior to taking oxygen permeability measurements, the lenses are hydrated by placing the lenses in isotonic buffered saline solution for at least eight hours. After hydration, if necessary because of handling, each lens is cleaned with MIRAFLW® Daily Cleaner (CIBA Vision Corporation, Duluth, Ga.) to remove grease and lipids prior to testing. Excess MIRAFLW® cleaner is removed by rinsing with saline or purified water.

Oxygen fluxes (J) are measured at 34 C in a wet cell (i.e., gas streams are maintained at about 100% relative humidity) using a Dk 1000 instrument. Oxygen transmissibility, D_k/t , is determined as outlined in the portions of the specification relating to oxygen permeability and transmissibility.

EXAMPLE A-2

A polysiloxane macromer is first prepared substantially in accordance with the procedure described in Example A-1.

A copolymer precursor solution is prepared by mixing about 180 grams polysiloxane-containing macromer, about 15 grams 3-methacryloxypropyltris (trimethylsiloxy)silane (Shin Etsu), about 4 grams 2-hydroxyethyl methacrylate ("HEMA"), about one gram ethylene glycol dimethacrylate ("EDGMA"), and about one gram DAROCUR® 1173 photoinitiator at room temperature for about 16 hours.

The copolymer precursor solution is then polymerized to form contact lenses. Polypropylene contact lens molds are filled with the copolymer precursor solution. Ultraviolet light (about 300 to 400 nm) at about 3–6 mW/cm² is applied to the solution in the mold for about 3 hours at room temperature. The UV light causes polymerization, thereby allowing the solution to form a contact lenses having the shape of the mold. The lens are extracted with isopropanol to remove remaining chloroform solvent and any unreacted components. A preferred resulting polymer contains about 81.8 weight percent polysiloxane macromer, about 13.6% TRIS, about 3.6% 2-hydroxyethyl methacrylate, and about 0.9% EDGMA.

The contact lens is degassed by placing the lens under suitable vacuum for a period sufficient to remove substantially all gas from the lens matrix. Fully hydrated degassed contact lenses having this composition have a Dk of about 87 barrers, a water content of about 19 weight percent, and a modulus of elasticity of about 2.5 MPa

EXAMPLE A-3

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 19.5 weight percent polysiloxane macromer, about 47% TRIS, and about 33.5% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 49 barrers, a water content of about 30 weight percent, and a modulus of elasticity of about 2.4 MPa.

EXAMPLE A4

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 50% TRIS, and about 20% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 76 barrers, a water content of about 20 weight percent, and a modulus of elasticity of about 1.3 MPa.

EXAMPLE A-5

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the

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final composition of about 30 weight percent polysiloxane macromer, about 40% TRIS, and about 30% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 55 barrers, a water content of about 30 weight percent, and a modulus of elasticity of about 3.5 MPa

EXAMPLE A-6

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 60% TRIS, and about 10% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 110 barrers, a water content of about 8.7 weight percent, and a modulus of elasticity of about 2.6 MPa

EXAMPLE A-7

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer and about 70% TRIS. Fully hydrated contact lenses having this composition have a Dk of about 128 barrers and a water content of about 4.9 weight percent.

EXAMPLE A-8

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 30 weight percent polysiloxane macromer, about 45% TRIS, 5% fluoroacrylate, and about 20% N,N-dimethylacrylamide. Fully hydrated contact lenses having this composition have a Dk of about 69 barrers, a water content of about 20 weight percent, and a modulus of elasticity of about 1.4 MPa.

EXAMPLE A-9

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 82 weight percent polysiloxane macromer, about 14.4% TRIS, and about 3.7% 2-hydroxyethyl methacrylate. Fully hydrated contact lenses having this composition have a Dk of about 96 barrers, a water content of about 19 weight percent, and a modulus of elasticity of about 1.8 MPa.

EXAMPLE A-10

A polysiloxane macromer is prepared substantially in accordance with the procedures described in Example A-1, but the polyethylene glycol has a molecular weight of about 660.

A contact lens is prepared substantially in accordance with the procedure described in Example 2, but having the final composition of about 81.9 weight percent polysiloxane macromer, about 13.6% TRIS, about 3.7% 2-hydroxyethyl methacrylate, and about 0.8% ethylene glycol dimethacrylate. Fully hydrated contact lenses having this composition have a Dk of about 81 barrers, a water content of about 20 weight percent, and a modulus of elasticity of about 1.4 MPa

EXAMPLE A-11

A contact lens is prepared substantially in accordance with the procedure described in Example A-2, but having the final composition of about 82 weight percent polysiloxane macromer, about 8.6% TRIS, about 4.9% fluoroacrylate,

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about 3.5% 2-hydroxyethyl methacrylate, and about 1% EDGMA. Fully hydrated contact lenses having this composition have a Dk of about 77 barrers, a water content of about 22 weight percent, and a modulus of elasticity of about 1.3 MPa

EXAMPLE A-12

A contact lens is prepared substantially in accordance with the procedure described in Example A-1, but the polysiloxane macromer used has hydroxy-sec-butyl end groups as opposed to hydroxyethylpropoxy end groups. The fully hydrated contact lens, after degassing, has a Dk of about 70 barrers, about a 22 weight percent water content, and a modulus of elasticity of about 2.4 Mpa.

EXAMPLE B-1

Macromer synthesis

51.5 g (50 mmol) of the perfluoropolyether Fomblin® ZDOL (from Ausimont S.p.A, Milan) having a mean molecular weight of 1030 g/mol and containing 1.96 meq/g of hydroxyl groups according to end-group titration is introduced into a three-neck flask together with 50 mg of dibutyltin dilaurate. The flask contents are evacuated to about 20 mbar with stirring and subsequently decompressed with argon. This operation is repeated twice. 22.2 g (0.1 mol) of freshly distilled isophorone diisocyanate kept under argon are subsequently added in a counterstream of argon. The temperature in the flask is kept below 30° C. by cooling with a waterbath. After stirring overnight at room temperature, the reaction is complete. Isocyanate titration gives an NCO content of 1.40 meq/g (theory: 1.35 meq/g).

202 g of the α,ω -hydroxypropyl-terminated polydimethylsiloxane KF-6001 from Shin-Etsu having a mean molecular weight of 2000g/mol (1.00 meq/g of hydroxyl groups according to titration) are introduced into a flask. The flask contents are evacuated to approx. 0.1 mbar and decompressed with argon. This operation is repeated twice. The degassed siloxane is dissolved in 202 ml of freshly distilled toluene kept under argon, and 100 mg of dibutyltin dilaurate (DBTDL) are added. After complete homogenization of the solution, all the perfluoropolyether reacted with isophorone diisocyanate (IPDI) is added under argon. After stirring overnight at room temperature, the reaction is complete. The solvent is stripped off under a high vacuum at room temperature. Microtitration shows 0.36 meq/g of hydroxyl groups (theory 0.37 meq/g). 13.78 g (88.9 mmol) of 2-isocyanatoethylmethacrylate (IEM) are added under argon to 247 g of the α,ω -hydroxypropyl-terminated polysiloxane-perfluoropolyether-polysiloxane three-block copolymer (a three-block copolymer on stoichiometric average, but other block lengths are also present). The mixture is stirred at room temperature for three days. Microtitration then no longer shows any isocyanate groups (detection limit 0.01 meq/g). 0.34 meq/g of methacryl groups are found (theory 0.34 meq/g).

The macromer prepared in this way is completely colourless and clear. It can be stored in air at room temperature for several months in the absence of light without any change in molecular weight.

EXAMPLE B-2

Macromer synthesis

The first step of the macromer synthesis described under Example B-1 is repeated. An isocyanate titration of the

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perfluoropolyether reacted with IPDI gives a content of 1.33 meq/g of NCO (theory 1.35 meq/g).

In a second step, 87.1 g of the α,ω -hydroxypropyl-terminated polydimethylsiloxane TegomerH-Si2111 (Th. Goldschmidt AG, Essen) having a mean molecular weight of 890 g/mol (2.25 meq/g of hydroxyl groups according to titration) are dissolved in 87 ml of toluene. After the reaction has been carried out as indicated under B-1 and the solvent has been removed, a hydroxyl group content of 0.66 meq/g is determined by microtitration (theory 0.60 meq/g). The resultant intermediate is in turn reacted with a stoichiometric amount of isocyanatoethyl methacrylate. Microtitration then no longer shows any isocyanate groups (detection limit 0.01 meq/g). 0.56 meq/g of methacryl groups are found (theory 0.53 meq/g). The macromer prepared in this way is completely colourless and clear and has a long shelf life.

EXAMPLE B-3

Macromer synthesis

The first step of the macromer synthesis described under Example B-1 is repeated, but using a different perfluoropolyether: Fomblin® ZDOLTX (from Ausimont S.p.A., Milan). This material is terminated by $\text{O}-\text{CF}_2-\text{CH}_2-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ (where $n=0, 1$ or 2). The material used has a mean molecular weight of 1146 g/mol, and contains 1.72 meq/g of hydroxyl groups according to end-group analysis. An isocyanate titration of the perfluoropolyether reacted with IPDI shows a content of 1.23 meq/g of NCO (theory 1.25 meq/g).

In the second step, a stoichiometric amount of Tegomer Hi-Si2111 and toluene are again added. After the reaction has been carried out as indicated under Example B-1 and the solvent has been removed, a hydroxyl group content of 0.63 meq/g is determined by microtitration (theory 0.58 meq/g). The resultant intermediate is in turn reacted with a stoichiometric amount of isocyanatoethyl methacrylate. Microtitration then no longer shows any isocyanate groups (detection limit 0.01 meq/g). 0.55 meq/g of methacryl groups are found (theory 0.51 meq/g). The macromer prepared in this way is completely colourless and clear and has a long shelf life.

EXAMPLE B4

Macromer synthesis

The first step of the macromer synthesis described under Example B-1 is repeated, but 5.0 g of Fomblin/ZDOL and 2.18 g of IPDI are employed. When the reaction is complete, microtitration shows an isocyanate group content of 1.31 meq/g of hydroxyl groups (theory 1.36 meq/g).

The second step of the synthesis described under Example B-1 is likewise carried out analogously, the stoichiometric ratio between isocyanate-terminated perfluoropolyether and hydroxypropyl-terminated polysiloxane being 2:3. After the reaction has been completed and the solvent has been removed, microtitration shows a content of 0.2 meq/g of hydroxyl groups (theory 0.18 meq/g).

The third step of the synthesis described under Example B-1 is likewise carried out analogously, IEM being employed in a precisely stoichiometric ratio. After the reaction, free isocyanate groups can no longer be detected (detection limit 0.01 meq/g). 0.19 meq/g of methacryl groups are found (theory 0.19 meq/g).

EXAMPLE B-5

Production of contact lenses

13.0 g of macromer from Example B-1 are dissolved in 5.6 g of ethanol (Fluka, puriss. p.a.) (70% by weight

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solution). After complete homogenization of the solution, 5.2 g of 3-tris(trimethylsiloxy)silylpropyl methacrylate (TRIS from Shin-Etsu, product No. KF-2801), 7.8 g of freshly distilled dimethylacrylamide (DMA) and 160 mg of photoinitiator Darocur® 1173 (Ciba) are added. This solution is filtered through a Teflon membrane having a pore width of 0.45 mm under an argon pressure of from 1 to 2 atm. The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert gas atmosphere, where the solution is pipetted into dust-free contact-lens moulds made from polypropylene. The moulds are closed, and the polymerization reaction is effected by UV irradiation (15 mW/cm², 5 min.), with simultaneous crosslinking. The moulds are then opened and placed in ethanol, causing the resultant lenses to swell out of the moulds. The lenses are extracted for 24 hours with constantly replenished distilled dichloromethane and subsequently dried in a high vacuum. The dried lenses are equilibrated in phosphate-buffered physiological saline solution in autoclave-resistant vials and then autoclaved at 120° C. for 30 minutes. All physical data measurements are carried out on autoclaved lenses.

The lenses produced in this way are characterized by the following values: oxygen permeability (Dk) 77 barrer (determined by the "wet" method described below), water content of the equilibrated lenses 32 percent by weight, elongation at break at 35° C. 360%, modulus of elasticity 30° C. 0.5 MPa (measured using a Minimat from Polymer Laboratories, UK).

"Wet" measurement of the oxygen permeability

The oxygen permeability of a material is determined by the coulometric method. To this end, pre-autoclaved lenses are clamped in a holder and then covered on the upper side with a 2 cm layer of water. A gas mixture comprising 21% of oxygen and 790% of nitrogen is passed continuously through the water layer with swirling. The oxygen which diffuses through the lens is measured using a coulometric detector. The reference values are those measured on commercially available contact lenses using this method. Ciba-soft® (CIBA-Vision, HEMA lens) gives a measurement of approx. 7-10 barrer, and Excelens® (CIBA-Vision, PVA lens) gives a measurement of approx. 22 barrer.

Unfortunately, the oxygen permeability of, for example, contact lenses is frequently given in the literature as a straight Dk value without further definition and frequently without giving any reference material. These are usually values determined on dry material (dry measurement). A comparative measurement of the oxygen permeability of polymer B-5 shows the differences:

- "wet" measurement: 77 barrer
- dry measurement: 158 barrer

EXAMPLE B6

The process described under Example B-5 for the production of contact lenses is repeated, but the mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 22.5% of DMA
- 0.5% of Blemer® QA

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EXAMPLE B-7

The process described under Example B-5 for the production of contact lenses is repeated, but the mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

EXAMPLE B-8

Analogously to EXAMPLE B-5 (in weight percent):

- 40% of macromer from Example B-1
- 30% of TRIS
- 30% of DMA

EXAMPLE B-9

The process described under B-5 for the production of contact lenses is repeated, but a 70% by weight solution of the macromer in toluene is used instead of the 75% by weight solution in ethanol described above. The mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

EXAMPLE B-10

The process described under B-5 for the production of contact lenses is repeated, but a 70% by weight solution of the macromer in octamethylcyclotetrasiloxane is used instead of the 75% by weight solution in ethanol described above. The mixture of comonomers has the following composition (in per cent by weight):

- 55% of macromer from Example B-1
- 22% of TRIS
- 23% of DMA

Physical measurement data for the contact-lens materials from Examples B-5 to B-10 (O₂ Dk value, wet method) are presented in TABLE B-I:

TABLE B-I

Example	Water Content (%)	Dk (barrer)	Modulus of Elasticity (MPa)	Elongation at Break (%)
B-5	32	77	0.5	360
B-6	23.8	110	1.1	160
B-7	19.5	110	0.6	130
B-8	30.9	81	0.3	300
B-9	30			
B-10	25			

EXAMPLE B-11

About 10.0 grams of macromer from Example B-1 are dissolved in 3.3 grams of ethanol (Fluka, puriss. p.a). After complete homogenization of the solution, about 4.0 grams of 3-tris(trimethylsiloxy)silylpropyl methacrylate (TRIS, from Shin-Etsu, product no. KF-2801), about 5.9 g. freshly distilled dimethylacrylamide (DMA), about 0.1 g. Blemer® QA (a methacrylate having quaternary ammonium substituents, Linz Chemie) and about 100 mg of photoinitiator Darocur® 1173 (Ciba) are added. The solution is

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filtered through a TEFLON membrane having a pore width of 0.45 mm under an argon pressure of from about 1 to 2 atm.

The filtered solution is frozen in a flask in liquid nitrogen, the flask is evacuated under a high vacuum, and the solution is returned to room temperature with the flask sealed. This degassing operation is repeated twice. The flask containing the macromer/comonomer solution is then transferred into a glove box with an inert gas atmosphere, where the solution is pipetted into dust-free, polypropylene contact lens molds. The molds are closed, and the polymerization reaction is effected by UV irradiation, with simultaneous crosslinking. The molds are then opened and placed in isopropyl alcohol, causing the resultant lenses to swell out of the molds. The lenses are extracted for about 24 hours with nearly continuous replenishing of isopropyl alcohol. Subsequently, the lenses are dried under high vacuum.

The dried contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. Physical measurement data for the autoclaved lens is presented below:

Dk [barrer]: 93
water content [%]: 20.3%
modulus of elasticity [Mpa]: 0.96

EXAMPLE B-12

Lenses are prepared in accordance with the procedures described in Example B-11, but are subsequent surface treated as follows. The dried lenses are transferred into a plasma coating apparatus wherein they are surface treated in a methane/"air" mixture ("air", as used here, denotes 79% nitrogen and 21% oxygen) for a period of about 5 minutes. The apparatus and plasma treatment process have been disclosed by H. Yasuda in "Plasma Polymerization", Academic Press, Orlando, Fla. (1985), pages 319 forward.

The plasma-treated contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. Physical measurement data for the plasma-coated autoclaved lens is presented below:

Dk [barrer]: 88
water content [%]: 21.8%
modulus of elasticity [Mpa]: 1.03

EXAMPLE B-13

Lenses are prepared in accordance with the procedures described in Example B-5, but the mixture of comonomers has the following composition, in weight percentages:

Macromer of Example B-1: 60%
TRIS: 25%
DMA: 15%

EXAMPLE B-14

Lenses are prepared in accordance with the procedures described in Example B-6, with the same comonomer composition, but the comonomers are dispensed into dust-free contact lens molds in ambient air atmosphere.

EXAMPLE C-1

Reaction of α,ω -bis-aminopropyl-dimethylpolysiloxane with D(+)-gluconic acid d-lactone:

Before the reaction, the amino-functionalized polydimethylsiloxane employed for the synthesis (X-22-161-C, Shin

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Etsu, JP) was finely dispersed in acetonitrile, extracted and then subjected to molecular distillation.

The following reactions take place with exclusion of H₂O. 200 g of purified amino-functionalized polydimethylsiloxane (0.375 meq of NH₂/g; Mn(VPO) 3400-3900 (VPO, Vapour Pressure Osmometry)), dissolved in 200 ml of absolute THF, are slowly added dropwise to a suspension of 13.35 g (75 mmol) of D(+)-gluconic acid d-lactone in 50 ml of absolute THF and the mixture is stirred at 40° C. for about 24 hours until the lactone has reacted completely. (Monitoring of the reaction by thin layer chromatography (TLC): silica gel; i-propanol/H₂O/ethyl acetate 6:3:1; staining with Ce(IV) sulfate/phosphoromolybdic acid solution (CPS reagent)). After the reaction, the reaction solution is concentrated to dryness and the residue is dried under 3 Pa (0.03 mbar) for 48 hours. 213.3 g of α,ω -bis(3-gluconamidopropyl)poly-dimethyl are obtained. Titration of the amino groups with perchloric acid shows a conversion of the amino groups of more than 99.8%.

Reaction of α,ω -bis-3-gluconamidopropyl-dimethylpolysiloxane with IEM

The product obtained above (213.3 g) is dissolved in 800 ml of absolute THF and the solution is heated to 40° C. with the addition of catalytic amounts of dibutyltin dilaurate (DBTDL). 14 g (90 mmol) of IEM in 20 ml of absolute THF are added dropwise to this solution over a period of about 4 hours. This corresponds to a concentration of 1.2 equivalents of IEM per gluconamide unit. The reaction is carried out in the course of 48 hours (monitoring of the reaction by IR spectroscopy detection of the NCO ties). The reaction solution is concentrated and the product is dried in a brown glass flask under 3 Pa (0.03 mbar) for 24 hours, while cooling with ice. 227.2 g of a colourless rubber-elastic product of high optical transparency remain.

EXAMPLE C-2 to C-7

Further amino propyl-dimethylpolysiloxanes (PDMS) are reacted with a different amount of gluconolactone and concentrations of IEM analogously to Example C-1. The examples are summarized in Table C-I

TABLE C-I

Ex-ample	Poly(dimethyl siloxane) (PDMS)			Amount of batch			
				PDMS g (mmol)	Glu g (mmol)	IEM g (mmol)	
	Name	Type	Mn	NH ₂ * of NH ₂			
C-1	X-22-161-C	term.	3400	2	200 (75)	13.4 (75)	14.0 (90.0)
C-2	X-22-161-C	term.	3400	2	200 (74)	13.4 (75)	25.7 (165.0)
C-3	X-22-161-C	term.	3400	2	200 (75)	13.4 (75)	29.2 (187.5)
C-4	PS 813	pen.	1200	1			
C-5	GP 4	pen.	3150	2.6			
C-6	GP 6	pen.	5960	3			
C-7	KF 8003	pen.	9700	4.7	200 (98)	17.5 (98)	18.2 (117.4)

Legend

X-22-161-C and KF 8003 are products from Shin Etsu (Japan), PS813 is a product from Petrarch-H Is, GP4 and GP6 are products from Genesee.

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* Amino groups per macromer chain
 Glu:D(+) gluconic acid d-lactone
 term: terminal
 pen: pendent

EXAMPLE C-8

The reaction is carried out in accordance with Example C-1, but instead of D(+)gluconic acid d-lactone, 75 mmol of lactobionic acid 1,5-lactone, suspended in 50 ml of absolute THF, are added dropwise to a solution of amino-functionalized polydimethylsiloxane (X-22-161-C) in 180 ml of absolute THF and 20 ml of DMSO (pure, 99%). Titration of the amino groups with perchloric acid indicates a reaction conversion of 99% (<0.01 meq of NH₂/g). Here also, a colourless optically clear macromer is obtained.

EXAMPLE C-9 and C-10

The reactions are carried out analogously to Example C-1. However, the catalyst necessary for addition of the isocyanate onto the hydroxyl groups is varied. Instead of DBTDL, catalytic amounts of 1,4-diazabicyclo(2.2.2)octane (DABCO) or 4 dimethylamino-pyridine (DMAP) are added and the reaction is continued as described under Example C-1. In both cases, an optically clear, colourless rubber-elastic macromer results in a manner corresponding to Example C-1.

EXAMPLE C-11

The reaction is carried out analogously to Example C-1. In a manner corresponding to Example C-8, 0.1 mol of lactobionic acid 1,5-lactone is suspended in 50 ml of absolute THF and the suspension is added dropwise to a solution of amino-functionalized polydimethylsiloxane (KF-8003) in 180 ml of absolute THF and 20 ml of DMSO (pure, 99%). The reaction time is increased to about 48 hours. A residual content of 0.07 meq of NH₂/g can be detected, and is reacted completely by addition of the corresponding molar amount of D(+)gluconic acid d-lactone to the reaction solution. The colourless highly transparent product has a residual content of amino groups of <0.01 meq/g.

EXAMPLE C-12

52.09 g (9.78 mmol) of purified amino-functionalized polydimethylsiloxane (X-22-161-C, Shin Etsu JP), dissolved in 110 ml of absolute THF, are initially introduced into the reaction vessel under an inert gas atmosphere, and 1.14 g (6.52 mmol) of D-glucaro-1,4:6,3-dilactone, dissolved in 20 ml of absolute THF, are added. The reaction solution is stirred at room temperature for 15 hours and then worked up in a manner corresponding to Example C-1. The amine content is 0.134 meq/g. The terminal amino groups of the resulting penta-block macromer are reacted with gluconolactone in the following reaction step. 41.84 g (5.146 meq of NH₂) of the above macromer and 0.917 g (5.15 mmol) of D(+)gluconic acid d-lactone are suspended in 300 ml of absolute THF and the suspension is stirred under nitrogen at 40° C. for 18 hours. The filtered solution is then concentrated and the residue is dried under 3 Pa (0.03 mbar) for 48 hours. A highly viscous optically clear substance having a residual content of amino groups of 0.013 meq/g results.

EXAMPLE C-13

Preparation of an amino- and perfluoroalkyl-functionalized polydimethylsiloxane

3.0 ml of absolute toluene are added to 15 g of poly(dimethylsiloxane-co-methylhydrosiloxane) (Bayer Silo-

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pren U-230; 10,000 g/mol; 2.3 mmol of Si—H/g), and 1.72 g (9.2 mmol) of allylphthalimide [CAS Reg. No. 5428-09-1] are then added. The mixture is frozen several times and the flask evacuated and then brought to room temperature again.

5 The flask is then let down with argon. 0.7 ml of a 0.005 molar solution of Lamoreaux catalyst (prepared in accordance with U.S. Pat. No. 3,220,972, General Electric) in absolute toluene (100 ppm of Pt/mol of Si—H) is added and the mixture is heated to 80° C. After a reaction time of half an hour, a colourless, clear to slightly cloudy solution, the 1H-NMR spectrum of which no longer shows resonances of allylic hydrogen atoms, is obtained.

Thereafter, 6.2 g (15.3 mmol) of degassed allyl 1H,1H, 2H,2H-perfluorooctyl ether are slowly added and the mixture is stirred at 80° C. for 2 hours. A 1H-NMR spectrum now shows a severely weakened resonance of the Si—H function at 4.6 ppm and an intense resonance at 0.5 ppm, which originates from Si—CH₂ hydrogen atoms.

3.0 ml of 1-hexene are then added in order to react the remaining excess of Si—H groups, which could otherwise cause crosslinking of the polymer when air later has access. The mixture is further stirred at 80° C. for another half an hour. The reaction mixture is then left to stand overnight. The product is purified over a silica gel column with hexane/ethyl acetate (3:2), the solvent is stripped off and the macromer is dried under a high vacuum. A colourless, clear, viscous product is obtained. The macromer purified in this way is taken up in 20 ml of hexane 20 ml of methylamine (33% in ethanol) are added and the mixture is heated to 40° C. After 10–15 minutes, a white voluminous precipitate separates out. After 30 minutes, the suspension is cooled and filtered and the precipitate is washed with a little hexane. The filtrate is evaporated and the residue is then dried under a high vacuum. Thereafter, the content of amino groups is determined by titrimetry (perchloric acid).

The resulting macromer is clear and viscous. The amino group content is 78.6% of theory. The total yield of macromer after the chromatographic purification is 75%.

Preparation of a gluconamide

17.3 g (corresponding to an amine content of 5.4 meq) of this aminoalkyl-substituted product are dissolved in 20 ml of dried THF. The solution is repeatedly frozen, degassed and let down with argon. All the following operations are carried out in an argon atmosphere. 712 mg of D(+)gluconic acid d-lactone (4 mmol) are then added. Because of the low solubility of the lactone, a suspension is initially obtained. After stirring overnight at 50° C., the solution is clear and the lactone has been used completely. The stoichiometric remaining amount of D(+)gluconic acid d-lactone (260 mg, 1.46 mmol) is then added and the mixture is stirred again at 50° C. overnight. A trace of unreacted lactone is observed. Completion of the reaction is monitored by means of thin layer chromatography on silica gel plates with the mobile phase 1-propanol/ethyl acetate/water (6:1:3). The silica gel plates are developed by means of Ce(IV) sulfate/phosphoromolybdic acid solution. Subsequent titration on amino groups yields a residual amino content of <0.1%. After filtration and removal of the solvent by distillation, a highly viscous clear macromer with 0.295 mequivalent of gluconamide per gram of macromer is obtained.

EXAMPLE C-14

Before the polymerization, the acrylates employed, isobutyl acrylate (IBA), N,N-dimethylacrylamide (DMA) and 3-methacryloyloxypropyl-tris(trimethylsilyloxy)silane (TRIS) are each freed from inhibitors by distillation. 0.32 g (2.76 mmol) of IBA, 0.80 g (8.1 mmol) of DMA and 1.44

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g (3.4 mmol) of TRIS are weighed into a 50 ml round-bottomed flask and the flask is flushed with N₂ for half an hour, while cooling with ice. 1.44 g of macromer from Example C-1 are transferred to a round-bottomed flask with a nitrogen attachment, degassed under 3 Pa (0.03 mbar) for 24 hours and then dissolved in 2.7 g of ethanol which has been flushed with N₂ for half an hour beforehand. The subsequent preparation of samples and the polymerization are carried out inside a glove box with exclusion of oxygen. The above monomer mixture and the macromer solution from Example C-1 are mixed, with the addition of 0.012 g (0.21 mmol) of Darocur® 1173 and the mixture is subjected to microfiltration (0.45 mm filter). 180 µl of this mixture are introduced into a polypropylene mould, which is then closed with an appropriate lid of polypropylene. The mixture is then irradiated with a UV-A mercury high pressure lamp in a nitrogen atmosphere in a UV oven equipped for this for 5 minutes. The lamps (5 each of the brand TLK40W/10R, Philips) are above and below the holder inserted. The irradiation intensity is 14.5 mW/cm².

The polypropylene mould is opened and the finished discs or lenses are removed by soaking by means of a solvent mixture of methylene chloride and ethanol (2:3). The lenses and discs are extracted in ethanol at room temperature in special polypropylene cages for 48 hours and then dried at 40° C. under 10 Pa (0.1 mbar) for 24 hours (autoclaving at 120° C., 30 minutes). The discs show an E modulus of 1.1 MPa, a permeability to oxygen of 183 barrier and a hardness (Shore A) of 53.

EXAMPLE C-15 to C-19

Further polymers are prepared in a manner corresponding to Example C-14 (composition in percentages by weight). Table C-II shows examples C-15 to C-19 and the properties of the resulting materials measured on discs.

TABLE C-II

Example	Water Content (%)	Macromer from Example	Macromer weight percent	DMA weight percent	DMEA weight percent	TRIS weight percent	E modulus (Mpa)	Dk (barrer)
C-15	not measured	C-3	32.8	—	30	37.2	—	—
C-16	19.9	C-3	32.9	34.3	—	32.7	0.7	84
C-17	25.1	C-3	39.3	34.3	—	36.4	0.9	72
C-18	17.5	C-3	35.7	34.3	—	30.0	0.7	100
C-19	23.4	C-3	33.3	33.3	—	33.4	0.7	96

Legend

DMA: N,N-Dimethylacrylamide

TRIS: 3-Methacryloyloxypropyl-tris(trimethylsilyloxy) silane

DMEA: 2-Dimethylaminoethyl acrylate

EXAMPLE C-20

Uncoated contact lens

A contact lens is prepared in a manner corresponding to Example C-14, using the Example C-3 macromer, with the following composition in percentages by weight:

Macromer: 33.3

DMA: 33.3

TRIS: 33.4

The lens has a Dk of about 94 and a water content of about 20.0 weight percent. The results are presented in TABLE C-III for comparison with coated lens properties.

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EXAMPLE C-21

Plasma-treated contact lens

Dried lenses prepared in accordance with the procedures described in Example C-20 are transferred into a plasma coating apparatus where the lenses are surface treated in a methane/"air" mixture ("air", as used here, denotes 79% nitrogen and 21% oxygen). The apparatus and plasma treatment process have been disclosed by H. Yasuda in "Plasma Polymerization", Academic Press, Orlando, Fla. (1985), pages 319 forward.

The dried plasma-treated contact lenses are equilibrated in autoclave-resistant vials in phosphate-buffered physiological saline solution, and then autoclaved for 30 minutes at about 120° C. The plasma-treated autoclaved lens has a Dk [barrer] of 90 and a water content of 21.5%. The results are presented in TABLE C-III for comparison with coated lens properties.

TABLE C-III

Example	Surface type	Dk (barrer)	Water content (%)
C-20	untreated	94	20.0
C-21	plasma-treated	90	21.5

EXAMPLE C-22

The synthesis of this polymer corresponds to Example C-14 with the following comonomer composition: Example C-3 macromer/TRIS/DMA: 32.8%/32.6%/34.2% (in percentages by weight) and an addition of 0.4% by weight of trimethylammonium-2-hydroxypropyl methacrylate hydrochloride (Blemer® QA, Nippon Oil Corp.). The polymer has a modulus of 0.9 MPa and a permeability to oxygen of 82 barrer. The water content is 25.1% (after 30 minutes' auto-

claving at 120° C.). For comparison, Example C-16 has a water content of 20% with a very similar comonomer composition (no addition of Blemer® QA).

EXAMPLE C-23

The polymer is prepared analogously to Example C-14, but the polymerization is carried out in bulk, which means without addition of ethanol. The composition of the comonomers and the material properties of the polymer synthesized, measured on discs is given below.

Example C-7 macromer: 41%

IBA: 23%

1-vinyl-2-pyrrolidone (NVP): 24%

acrylonitrile (AN): 12%

Hardness (shore A): 68

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EXAMPLE C-24

The polymerization is carried out in accordance with Example C-14 but with the following changed comonomer composition:

macromer of Example C-7/IBA/TRIS 20%/90%/60% and 1% (in percentages by weight) of bis(3-methacryloyloxypropyl)tetra methylsiloxane.

An optically clear polymer with an E modulus of 0.4 MPa, a permeability to oxygen of 241 barrer and a hardness (Shore A) of 42 is obtained.

EXAMPLES C-25 through C-27

Contact lenses are prepared in accordance with the procedure described in Example C-14. The compositions in weight percentages are as follows:

Example	Macromer	Macromer weight percent	IBA weight percent	DMA weight percent	TRIS weight percent	HFBA weight percent
C-25	C-3	36.0	8.0	20.0	36.0	—
C-26	C-2	35.0	5.0	20.0	35.0	5.0
C-27	C-3	32.8	—	30.0	37.2	—

where

IBA is isobutylacrylate,

DMA is N,N-Dimethylacrylamide

TRIS is 3-methacryloyloxypropyl-tris(trimethylsiloxy) silane

HFBA is 2,2,3,4,4,4-hexafluorobutylacrylate

EXAMPLE C-28

The polymerization is carried out in accordance with Example C-14 but with the following changed comonomer composition: macromer of Example C-1/DMA/TRIS 33.3%/33.3%/33.3%. An optically clear polymer is obtained.

EXAMPLE D-1

Macromer Synthesis

In a dry box under nitrogen atmosphere, about 200 grams of dry PDMS dipropoxyethanol (Shin-Etsu) is added to a container. Isocyanatoethyl methacrylate (IEM) in an amount equal to about 2 moles per mole PDMS dialkanol is added to the container. About 0.1 weight percent dibutyltin dilaurate (DBTL) catalyst, based on PDMS dialkanol weight, is added to the container along with a stir bar. The container is immersed in an oil bath atop a stir plate, and secured in place with a clamp. A stream of UPC air at about 2 psig is passed over the mixture. The mixture is agitated at room temperature (about 22° C.) for about 24 hours. An iterative procedure follows in which the mixture is analyzed for isocyanate content and IEM is added if the PDMS dialkoxyalkanol has not been completely reacted. The mixture is stirred about 24 hours more. The macromer produced is a siloxane-containing macromer.

EXAMPLE D-2

Lens fabrication

A prepolymerization mixture is prepared by mixing about 56 grams of the macromer from Example D-1, about 14 grams of TRIS, about 29 grams N,N -dimethylacrylamide

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(DMA), about 1 gram methacrylic acid, about 0.5 grams Darocur® 1173 photoinitiator, and about 20 grams hexanol. The mixture is agitated for about 20 minutes at room temperature.

Next, the mixture is degassed via a series of freezing and thawing steps. The container is placed in a liquid nitrogen bath until the mixture solidifies. A vacuum is applied to the container at a pressure of about 200 millitorr or less for about 5 minutes. Then, the container is placed in a bath of room temperature water until the mixture is liquid again. This process is performed a total of three times.

The mixture is then polymerized to form contact lenses. The prepolymerization mixture is poured into polypropylene contact lens molds in a nitrogen atmosphere. The polymerization is effected by applying UV radiation (about 4–6 mW/cm²) for a period of about 15 minutes.

The resulting fully hydrated contact lens has a water content of about 23%. The lens has a Dk of about 115 barrers and a modulus of elasticity of about 2 MPa

EXAMPLE D-3

Lens fabrication

A contact lens is prepared in accordance with the procedure described in Example D-2, with the difference being that the composition is about 50% macromer of Example D-1, about 20% TRIS and about 30% DMA.

The resulting fully hydrated contact lens has a water content of about 20%. The lens has a Dk of about 118 barrers and a modulus of elasticity of about 1.8 Mpa.

EXAMPLE E-1

Material A

A contact lens is prepared substantially in accordance with the procedure described in Example A-2. Prior to polymerization, the prepolymerization mixture is degassed by cooling the prepolymer mixture with liquid nitrogen until the mixture solidifies and is near liquid nitrogen temperature, then applying a vacuum (about 0.1 mm Hg) to the solidified prepolymer mixture, discontinuing the vacuum, and thawing the prepolymer mixture until the mixture is again in liquid form. This degassing procedure is performed a total of three times on the prepolymerization mixture.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 19%. Subsequent to curing, the lens is plasma treated for about 10 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume:volume ratio. The working pressure of the gas is about 50 millitorr. The plasma treatment is accomplished in a Plasma Polymerization Apparatus LCVD-20-400A (Plasmacarb, Bedford, Mass.).

The Ionoton Ion Permeability Coefficient of the lens is 0.81×10⁻³ cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-2

Material B

A contact lens is prepared substantially in accordance with the procedure described in Example B-10. Prior to polymerization, nitrogen gas is bubbled through the prepolymer mixture in order to remove oxygen from the prepolymer mixture.

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The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 26 weight percent. No coating is applied to the surface.

The Ionoton Ion Permeability Coefficient of the lens is $-0.063 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

EXAMPLE E-3**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 3 minutes in an atmosphere of methane and air at a 2:1 CH_4 :air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is $0.50 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-4**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH_4 :air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is $0.47 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-5**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-12. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH_4 :air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is $0.35 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-6**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-11. Prior to

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polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. The cured lens has an equilibrium water content of about 30 weight percent. The lens is not subsequently coated.

The Ionoton Ion Permeability Coefficient of the lens is $1.1 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-7**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-21. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH_4 :air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is $2.9 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-8**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-21. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH_4 :air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is $0.25 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-9**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-20. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in an air atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

The Ionoton Ion Permeability Coefficient of the lens is $0.008 \times 10^{-3} \text{ cm}^2/\text{sec}$. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

EXAMPLE E-10**Material D**

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

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The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

The Ionoton Ion Permeability Coefficient of the lens is 1.4×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-11**Material D**

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 7.5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

The Ionoton Ion Permeability Coefficient of the lens is 0.61×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

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The Ionoton Ion Permeability Coefficient of the lens is 1.5×10^{-3} cm²/sec. Clinical examination shows that the lens moves on the human eye. See Table E for a summary of the results.

EXAMPLE E-13**Material D**

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in an air atmosphere to form the contact lens. Subsequent to curing, the lens is not surface treated.

The Ionoton Ion Permeability Coefficient of the lens is -0.001×10^{-3} cm²/sec. Clinical examination shows that the lens does not move on the human eye. See Table E for a summary of the results.

TABLE E

Example	Material	Degassing	Curing atmosphere	Surface treatment CH ₄ :air plasma (minutes)	Ionoton Ion Permeability Coefficient (10 ⁻³ cm ² /sec)	On-eye Movement
E-1	A	3-cycle freeze/thaw	nitrogen	10	0.81	YES
E-2	B	nitrogen bubble	nitrogen	no plasma	-0.063	NO
E-3	B	3-cycle freeze/thaw	nitrogen	3	0.50	YES
E-4	B	3-cycle freeze/thaw	nitrogen	5	0.47	YES
E-5	B	3-cycle freeze/thaw	nitrogen	7.5	0.35	YES
E-6	B	3-cycle freeze/thaw	nitrogen	no plasma	1.1	YES
E-7	C	3-cycle freeze/thaw	nitrogen	5	2.9	YES
E-8	C	3-cycle freeze/thaw	nitrogen	7.5	0.25	YES
E-9	C	3-cycle freeze/thaw	air	no plasma	0.008	NO
E-10	D	3-cycle freeze/thaw	nitrogen	no plasma	1.4	YES
E-11	D	3-cycle freeze/thaw	nitrogen	7.5	0.61	YES
E-12	D	3-cycle freeze/thaw	nitrogen	5	1.5	YES
E-13	D	3-cycle freeze/thaw	air	no plasma	-0.001	NO

EXAMPLE E-12**Material D**

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. Prior to polymerization, the prepolymerization mixture is degassed by the repeated freeze/thaw procedure of Example E-1.

The prepolymer mixture is cured in a nitrogen atmosphere to form the contact lens. Subsequent to curing, the lens is plasma treated for about 5 minutes in an atmosphere of methane and air at a 2:1 CH₄:air volume ratio.

Considering Examples E-1 through E-13 of Table E, the lowest value of Ionoton Ion Permeability Coefficient for which a lens moves on the eye is 0.25×10^{-3} cm²/sec. The highest value of Ionoton Ion Permeability Coefficient for a lens which bound on the eye is 0.008×10^{-3} cm²/sec. Thus, a contact lens preferably has an Ionoton Ion Permeability Coefficient greater than about 0.008×10^{-3} cm²/sec., more preferably greater than about 0.25×10^{-3} cm²/sec.

EXAMPLE F-1**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-25. Prior to

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surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 0 mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone (PVP) in accordance with the following procedure, using a glass plasma reactor equipped with an external ring electrode and a 27.13 MHz radio frequency (RF) generator for the generation of an inductively-coupled, cold glow discharge plasma. Highly purified argon is used as a plasma gas and as a carrier gas for N-vinylpyrrolidone (NVP) monomer feed. The NVP feed line is located about 10 cm below the glow zone.

The contact lens is placed in the 20 cm diameter plasma reactor at a position about 15 cm below the plasma glow zone. The reactor is then evacuated for about 30 minutes to about 0.009 mbar. Subsequent to evacuation, the plasma gas flow is set to 20 sccm (standard cubic centimeters), the glow discharge is started at a pressure of about 0.15 mbar and maintained for about one minute at a power of about 170 Watts (in order to clean and activate the lens surface). After reduction of argon plasma gas flow to about 10 sccm, the argon carrier gas flow for the NVP monomer is also set to 10 sccm. The temperature of the NVP source (with the carrier gas bubbling through the liquid NVP) is held at about 40° C. The lenses are treated for about 10 minutes with a pulsing glow discharge plasma (1 μsec. on, 3 μsec. off) at about 0.35 mbar pressure and about 150 Watts power.

After interrupting the glow discharge and the carrier gas flow, the reactor is continuously purged with a 20 sccm argon steam at a pressure of about 0.009 mbar for about 30 minutes, in order to remove residual monomer and activated species. The PVP coated contact lenses thus produced are highly wettable and show the following dynamic contact angles, measured with a KRUESS (Hamburg, Germany) K-12 instrument:

	Untreated	Treated
Advancing	102	38
Receding	48	23
Hysteresis	53	15

Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-2**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-26. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.8×10^{-7} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-3**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-27. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 9.3×10^{-7} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example

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F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-4**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-18. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.6×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-5**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-16. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.3×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-6**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-19. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 2.7×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-7**Material C**

A contact lens is prepared substantially in accordance with the procedure described in Example C-17. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 7.8×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-8**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-13. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.5×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-9**Material B**

A contact lens is prepared substantially in accordance with the procedure described in Example B-14. Prior to

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surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 1.1×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens does not move on the eye. See Table F for a summary of the results.

EXAMPLE F-10

Material B

A contact lens is prepared substantially in accordance with the procedure described in Example B-7. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 3.8×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-11

Material B

A contact lens is prepared substantially in accordance with the procedure described in Example B-6. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 8.5×10^{-6} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

EXAMPLE F-12

Material B

A contact lens is prepared substantially in accordance with the procedure described in Example B-5. Prior to surface treatment, the Ionoflux Ion Permeability Coefficient is determined to be about 7.1×10^{-5} mm²/min.

Subsequent to ion permeability measurements, the lens surface is coated with polyvinylpyrrolidone as in Example F-1. Clinical tests show that the lens moves on the eye. See Table F for a summary of the results.

TABLE F

EXAMPLE	MATERIAL (Example reference number)	IONOFLUX ION PERMEABILITY COEFFICIENT* (mm ² /min)	ON-EYE MOVEMENT- CLINICAL DETERMINATION
F-1	C-25	0	NO
F-2	C-26	0.28×10^{-6}	NO
F-3	C-27	0.93×10^{-6}	NO
F-4	C-18	2.6×10^{-6}	YES
F-5	C-16	13.0×10^{-6}	YES
F-6	C-19	27.0×10^{-6}	YES
F-7	C-17	7.8×10^{-6}	YES
F-8	B-13	1.5×10^{-6}	NO
F-9	B-14	1.1×10^{-6}	NO
F-10	B-7	3.8×10^{-6}	YES
F-11	B-6	8.5×10^{-6}	YES
F-12	B-5	71.0×10^{-6}	YES

*All Ionoflux Ion Permeability Coefficients were determined on uncoated lenses.

Considering only Examples F-1 through F-13 of Table F, the lowest value of Ionoflux Ion Permeability Coefficient for which a lens moves on the eye is 2.6×10^{-6} mm²/min. The highest value of Ionoflux Ion Permeability Coefficient for a lens which binds on the eye is 1.5×10^{-6} mm²/min. Thus, a

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contact lens preferably has an Ionoflux Ion Permeability Coefficient greater than about 1.5×10^{-6} mm²/min., more preferably greater than about 2.6×10^{-6} mm²/min.

EXAMPLE G-1

A contact lens is prepared substantially in accordance with the procedure described in Example A-2. The Hydrodell Water Permeability Coefficient is determined to be about 0.71×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-2

A contact lens is prepared substantially in accordance with the procedure described in Example B-5. The Hydrodell Water Permeability Coefficient is determined to be about 1.09×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-3

A contact lens is prepared substantially in accordance with the procedure described in Example B-6. The lens is surface treated in a plasma gas in accordance with the procedure described in Example F-1. The Hydrodell Water Permeability Coefficient is determined to be about 0.27×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-4

A contact lens is prepared substantially in accordance with the procedure described in Example C-19. The lens is surface treated in a plasma gas in accordance with the procedure described in Example F-1. The Hydrodell Water Permeability Coefficient is determined to be about 0.37×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-5

A contact lens is prepared substantially in accordance with the procedure described in Example D-2. The Hydrodell Water Permeability Coefficient is determined to be about 1.26×10^{-6} cm²/second. Clinical tests show that the lens moves on the eye. See Table G for a summary of the results.

EXAMPLE G-6

A contact lens is prepared substantially in accordance with the procedure described in Example C-14. The Hydrodell Water Permeability Coefficient is determined to be about 0.08×10^{-6} cm²/second. Clinical tests show that the lens does not move on the eye. See Table G for a summary of the results.

TABLE G

EX- AMPLE	MATERIAL (Example reference number)	SURFACE TREAT- MENT	HYDRODELL WATER PERMEABILITY COEFFICIENT (cm ² /sec.)	ON-EYE MOVEMENT- CLINICAL DETER- MINATION
G-1	A-2	none	0.71×10^{-6}	YES
G-2	B-5	none	1.09×10^{-6}	YES
G-3	B-6	PVP	0.27×10^{-6}	YES
G-4	C-19	PVP	0.37×10^{-6}	YES

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TABLE G-continued

EX- AMPLE	MATERIAL (Example reference number)	SURFACE TREAT- MENT	HYDRODELL WATER PERMEABILITY COEFFICIENT (cm ² /sec.)	ON-EYE MOVEMENT- CLINICAL DETER- MINATION
G-5	D-2	none	1.26×10^{-6}	YES
G-6	C-14	none	0.08×10^{-6}	NO

Considering only Examples G-1 through G-6 of Table G, the lowest value of Hydrodell Water Permeability Coefficient for which a lens moves on the eye is 0.27×10^{-6} cm²/sec. The highest value of Hydrodell Water Permeability Coefficient for a lens which binds on the eye is 0.08×10^{-6} cm²/sec. Thus, a contact lens preferably has a Hydrodell Water Permeability Coefficient greater than about 0.08×10^{-6} cm²/sec., more preferably greater than 0.27×10^{-6} cm²/sec.

The invention has been described in detail, with reference to certain preferred embodiments, in order to enable the reader to practice the invention without undue experimentation. Theories of operation have been offered to better enable the reader to understand the invention, but such theories do not limit the scope of the invention. In addition, a person having ordinary skill in the art will readily recognize that many of the previous components, compositions, and parameters may be varied or modified to a reasonable extent without departing from the scope and spirit of the invention. Furthermore, titles, headings, example materials or the like are provided to enhance the reader's comprehension of this document, and should not be read as limiting the scope of the present invention. Accordingly, the intellectual property rights to the invention are defined by the following claims, reasonable extensions and equivalents thereof, as interpreted in view of the disclosure herein.

That which is claimed is:

1. An ophthalmic lens, comprising an inner and outer surface, wherein said inner surface is adapted to rest immediately adjacent to the human cornea, wherein said lens has the following properties:

- (a) an oxygen permeability from said inner to said outer surface sufficient to prevent substantial corneal swelling during a period of extended wear;
- (b) ophthalmic compatibility during a period of extended, continuous, intimate contact with the ocular environment; and
- (c) ion or water permeability sufficient to allow lens movement on the eye in an amount sufficient to sustain corneal health and wearer comfort,

wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about 0.2×10^{-6} cm²/sec or (2) an Ionoflux Diffusion Coefficient of greater than about 1.5×10^{-6} cm²/min, wherein said ion permeability is measured with respect to sodium ions.

2. An ophthalmic lens of claim 1, wherein said period of extended wear is at least 24 hours.

3. An ophthalmic lens of claim 2, wherein said lens produces, after wear of about 24 hours, including normal sleep periods, less than about 8% corneal swelling.

4. An ophthalmic lens of claim 3, wherein said lens produces, after wear of about 24 hours, including normal sleep periods, less than about 6% corneal swelling.

5. An ophthalmic lens of claim 4, wherein said lens produces, after wear of about 24 hours, including normal sleep periods, less than about 4% corneal swelling.

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6. An ophthalmic lens of claim 2, wherein said extended period of wear is at least 4 days.

7. An ophthalmic lens of claim 6, wherein said extended period of wear is at least 7 days.

8. An ophthalmic lens of claim 7, wherein said lens produces, after wear of about 7 days, including normal sleep periods, less than about 10% corneal swelling.

9. An ophthalmic lens of claim 8, wherein said lens produces, after wear of about 7 days, including normal sleep periods, less than about 7% corneal swelling.

10. An ophthalmic lens of claim 9, wherein said lens produces, after wear of about 7 days, including normal sleep periods, less than about 5% corneal swelling.

11. An ophthalmic lens of claim 1, wherein said period of extended wear is at least 14 days.

12. An ophthalmic lens of claim 11, wherein said extended period of wear is at least 30 days.

13. An ophthalmic lens of claim 1, wherein said oxygen permeability (Dk) is at least 80 barrers/mm.

14. An ophthalmic lens of claim 1, wherein said lens has a tensile modulus of 1.5 MPa or less.

15. An ophthalmic lens of claim 1, wherein said lens has a short relaxation time constant of greater than about 3.5 seconds.

16. An ophthalmic lens of claim 1, wherein the lens has a tan δ above about 0.25 at about 10 Hz.

17. An ophthalmic lens of claim 1, wherein said lens has an Ionoton Ion Permeability Coefficient of at least about 0.3×10^{-6} cm²/sec.

18. An ophthalmic lens of claim 1, wherein said lens has an Ionoflux Diffusion Coefficient of greater than about 2.6×10^{-6} cm²/min.

19. An ophthalmic lens of claim 1, wherein said lens has a Hydrodell Water Permeability Coefficient of greater than about 0.2×10^{-6} cm²/sec.

20. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 24 hours and said oxygen transmissibility is at least 80 barrers/min, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of 1.4 to 10 seconds, and an Ionoton Ion Permeability Coefficient of at least 0.2×10^{-6} cm²/sec.

21. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 4 days and said oxygen permeability (Dk) is at least 90 barrers/mm, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and an Ionoton Ion Permeability Coefficient of at least 0.4×10^{-6} cm²/sec.

22. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 4 days and said oxygen permeability (Dk) is at least 90 barrers/mm, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and an Ionoflux Diffusion Coefficient of greater than about 1.5×10^{-6} mm²/min.

23. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 4 days and said oxygen permeability (Dk) is at least 90 barrers/mm, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and a Hydrodell Water Permeability Coefficient of greater than about 0.2×10^{-6} cm²/sec.

* * * * *

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REEXAMINATION CERTIFICATE (4205th)

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Nicolson et al. [45] Certificate Issued Nov. 14, 2000

[54] EXTENDED WEAR OPHTHALMIC LENS

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[58] Field of Search **523/106, 107;**
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Primary Examiner—Vasudevan S. Jagannathan

[57] ABSTRACT

An ophthalmic lens suited for extended-wear for periods of
 at least one day on the eye without a clinically significant
 amount of corneal swelling and without substantial wearer
 discomfort. The lens has a balance of oxygen permeability
 and ion or water permeability, with the ion or water perme-
 ability being sufficient to provide good on-eye movement,
 such that a good tear exchange occurs between the lens and
 the eye. A preferred lens is a copolymerization product of a
 oxyperm macromer and an ionoperm monomer. The invention
 encompasses extended wear contact lenses, which
 include a core having oxygen transmission and ion trans-
 mission pathways extending from the inner surface to the
 outer surface.

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Defendant Bausch & Lomb Incorporated’s Opposition to CIBA Corporation’s Motion to Use Evidence from this case at the Reexamination Proceedings (with Exhibits A–J) (Note: This Information is Subject to Protective Order—Not Open to Public, Only by Examiner or Other Authorized Patent and Trademark Office Employee).

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REEXAMINATION CERTIFICATE ISSUED UNDER 35 U.S.C. 307

THE PATENT IS HEREBY AMENDED AS
INDICATED BELOW.

Matter enclosed in heavy brackets [] appeared in the patent, but has been deleted and is not longer a part of the patent; matter printed in italics indicates additions made to the patent.

ONLY THOSE PARAGRAPHS OF THE
SPECIFICATION AFFECTED BY AMENDMENT
ARE PRINTED HEREIN.

Column 11, lines 45–53:

An Ionoflux Diffusion Coefficient of greater than about 1.5×10^{-6} mm²/min is preferred for achieving sufficient on-eye movement. More preferably, the Ionoflux Diffusion Coefficient is greater than about 2.6×10^{-6} mm²/min, while most preferably, the Ionoflux Diffusion Coefficient is greater than about 6.4×10^{-6} mm²/min. It must be emphasized that the Ionoflux Diffusion Coefficient correlates with ion permeability through the lens, and thereby is a predictor of on-eye movement.

AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

Claim 2 is cancelled.

Claims 1, 3, 6, 13 and 21–23 are determined to be patentable as amended.

Claims 4, 5, 7–12 and 14–20, dependent on an amended claim, are determined to be patentable.

New claims 24–30 are added and determined to be patentable.

1. An ophthalmic lens [] having a surface modified by a surface treatment process, said lens comprising an inner and outer surface, wherein said inner surface is adapted to rest immediately adjacent to the human cornea, wherein said lens has the following properties:

- (a) an oxygen permeability from said inner to said outer surface sufficient to prevent substantial corneal swelling during a period of extended wear;
- (b) ophthalmic compatibility during a period of extended, continuous, intimate contact with the ocular environment while having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of wear of at least 24 hours; and
- (c) ion or water permeability sufficient to allow lens movement on the eye in an amount sufficient to sustain corneal health and wearer comfort,

wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized either by (1) an Ionoton Ion Permeability Coefficient of greater than about 0.2×10^{-6} cm²/sec or (2) an Ionoflux Diffusion Coefficient of greater than about 1.5×10^{-6} mm²/min, wherein said ion permeability is measured with respect to sodium ions.

3. An ophthalmic lens of claim [2] 1, wherein said lens produces, after wear of about 24 hours, including normal sleep periods, less than about 8% corneal swelling.

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6. An ophthalmic lens of claim [2] 1, wherein said extended period of wear is at least 4 days.

13. An ophthalmic lens of claim 1, wherein said oxygen permeability (Dk) is at least 80 [barrers/mm] barrers.

21. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 4 days and said oxygen permeability (Dk) is at least 90 [barrers/mm] barrers, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and an Ionoton Ion Permeability Coefficient of at least 0.4×10^{-6} cm²/sec.

22. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 4 days and said oxygen permeability (Dk) is at least 90 [barrers/mm] barrers, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and an Ionoflux Diffusion Coefficient of greater than about 1.5×10^{-6} mm²/min.

23. An ophthalmic lens of claim 1, wherein said extended period of wear is at least 4 days and said oxygen permeability (Dk) is at least 90 [barrers/mm] barrers, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and a Hydrotell Water Permeability Coefficient of greater than about 0.2×10^{-6} cm²/sec.

24. An ophthalmic lens having a surface modified by a surface treatment process, said lens comprising an inner and outer surface, wherein said inner surface is adapted to rest immediately adjacent to the human cornea, wherein said lens has the following properties:

- (a) an oxygen permeability from said inner to said outer surface sufficient to prevent substantial corneal swelling during a period of extended wear;
 - (b) ophthalmic compatibility during a period of extended, continuous, intimate contact with the ocular environment while having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of wear of at least 24 hours; and
 - (c) ion or water permeability sufficient to allow lens movement on the eye in an amount sufficient to sustain corneal health and wearer comfort,
- wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized by an Ionoton Ion Permeability Coefficient of greater than about 8.0×10^{-6} cm²/sec, wherein said ion permeability is measured with respect to sodium ions.

25. An ophthalmic lens comprising an inner and outer surface, wherein said inner surface is adapted to rest immediately adjacent to the human cornea, wherein said lens has the following properties:

- (a) an oxygen permeability equal to or greater than 69 barrers from said inner to said outer surface sufficient to prevent substantial corneal swelling during a period of extended wear;
- (b) ophthalmic compatibility during a period of extended, continuous, intimate contact with the ocular environment while having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of wear of at least 24 hours; and

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(c) ion or water permeability sufficient to allow lens movement on the eye in an amount sufficient to sustain corneal health and wearer comfort,

wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized by an Ionoton Ion Permeability Coefficient of greater than about $250.0 \times 10^{-6} \text{ cm}^2/\text{sec}$, wherein said ion permeability is measured with respect to sodium ions, and

wherein said lens is autoclaved without lowering either said oxygen permeability or said ion permeability below levels sufficient to maintain good corneal health and on-eye movement.

26. An ophthalmic lens comprising a core material surrounded, at least in part, by a surface modified by a surface treatment process, said lens comprising an inner and outer surface, wherein said inner surface is adapted to rest immediately adjacent to the human cornea, wherein said lens has the following properties:

(a) an oxygen permeability equal to or greater than 69 barrers from said inner to said outer surface sufficient to prevent substantial corneal swelling during a period of extended wear;

(b) ophthalmic compatibility during a period of extended, continuous, intimate contact with the ocular environment while having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of wear of at least 7 days; and

(c) ion or water permeability sufficient to allow lens movement on the eye in an amount sufficient to sustain corneal health and wearer comfort,

wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized by an Ionoton Ion Permeability Coefficient of greater than about $350.0 \times 10^{-6} \text{ cm}^2/\text{sec}$, wherein said ion permeability is measured with respect to sodium ions.

27. An ophthalmic lens of claims 24, or 25, wherein said extended period of wear is at least 4 days and said oxygen

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transmissibility is at least 80 barrers/mm, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of 1.4 to 10 seconds, and an Ionoton Ion Permeability Coefficient of at least $350.0 \times 10^{-6} \text{ cm}^2/\text{sec}$.

28. An ophthalmic lens having a surface modified by a surface treatment process, said lens comprising an inner and outer surface, wherein said inner surface is adapted to rest immediately adjacent to the human cornea, wherein said lens has the following properties:

(a) an oxygen permeability equal to or greater than about 72 barrers from said inner to said outer surface sufficient to prevent substantial corneal swelling during a period of extended wear;

(b) ophthalmic compatibility during a period of extended, continuous, intimate contact with the ocular environment while having adequate movement on the eye with blinking to promote adequate tear exchange and without producing significant corneal swelling, without having substantial amounts of lipid adsorption, and without causing substantial wearer discomfort during the period of wear of at least 7 days; and

(c) ion or water permeability sufficient to allow lens movement on the eye in an amount sufficient to sustain corneal health and wearer comfort,

wherein said ophthalmic lens has an oxygen transmissibility of at least about 70 barrers/mm and an ion permeability characterized by an Ionoflux Diffusion Coefficient of greater than about $1.5 \times 10^{-6} \text{ mm}^2/\text{min}$, wherein said ion permeability is measured with respect to sodium ions.

29. An ophthalmic lens of claim 28, wherein said lens has an Ionoflux Diffusion Coefficient of greater than about $2.6 \times 10^{-6} \text{ mm}^2/\text{min}$.

30. An ophthalmic lens of claims 28 or 29, wherein said extended period of wear is at least 30 days and said oxygen permeability (Dk) is at least 90 barrers, and wherein said lens has a tensile modulus of 1.5 MPa or less, a short relaxation time constant of greater than about 3.5 seconds, and an Ionoflux Diffusion Coefficient of greater than about $6.4 \times 10^{-6} \text{ mm}^2/\text{min}$.

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